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H_3^{++} molecular ion in a strong magnetic field: triangular configuration

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Abstract

The existence of the molecular ion H_3^{++} in a magnetic field in a triangular configuration is revised. A variational method with an optimization of the form of the vector potential (gauge fixing) is used. It is shown that in the range of magnetic fields $10^8 < B < 10^{11}\,G$ the system ($pppe$), with the protons forming an equilateral triangle perpendicular to the magnetic line, has a well-pronounced minimum in the total energy. This configuration is unstable under the decays H-atom $+ p + p$ and $H_2^+ + p$. The triangular configuration of H_3^{++} complements H_3^{++} in the linear configuration which exists for $B \gtrsim 10^{10}\,G$.

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I. INTRODUCTION

Recently, it was announced that the molecular ion H_3^{++} in a linear configuration can exist in a strong magnetic field $B \gtrsim 10^{10}\,G$ and become even the most stable one-electron system at $B \gtrsim 10^{13}\,G$ [2, 3]. The goal of this article is to study whether the H_3^{++} molecular ion can exist in a certain spatial configuration – the protons form an equilateral triangle while a magnetic field is directed perpendicular to it. This configuration was already studied in [1] with an affirmative answer. In the present work we will show that an improper gauge dependence of the trial functions in [1] caused a significant loss of accuracy and led to qualitatively incorrect results.

The Hamiltonian which describes three infinitely heavy protons and one electron placed in a uniform constant magnetic field directed along the $z-$axis, $\mathbf{B} = (0, 0, B)$ is given by

$$\mathcal{H} = \hat{p}^2 + \frac{2}{R_{ab}} + \frac{2}{R_{ac}} + \frac{2}{R_{bc}} - \frac{2}{r_1} - \frac{2}{r_2} - \frac{2}{r_3} + 2(\hat{p}\mathcal{A}) + \mathcal{A}^2 \ , \tag{1}$$

(see Fig.1 for notations), where $\hat{p} = -i\nabla$ is the momentum, $\mathcal{A}$ is a vector potential, which corresponds to the magnetic field $\mathbf{B}$. We assume that the protons a, b, c form an equilateral triangle, $R_{ab} = R_{bc} = R_{ac} = R$, and the magnetic field $\mathbf{B}$ is directed perpendicular to it. This configuration of the protons is stable from classical-mechanical point of view, since electrostatic repulsion of the protons is compensated by the Lorentz force. It justifies more the use of the Born-Oppenheimer approximation and also adds extra stability to the whole system ($pppe$). A small perturbation of a proton position directed outside the plane perpendicular to the magnetic line can distort the above triangular configuration. However, our calculations show that the presence of the electron can stabilize the configuration, at least, for small perturbations. Thus, the stability of this configuration is of a different nature than the linear one. There it appears to be a consequence of the quasi-one-dimensionality of the problem and the compensation of the proton repulsion by the interaction with one-dimensional electronic cloud [2, 3].

Atomic units are used throughout ($\hbar$=m_e=e=1) albeit energies are expressed in Rydbergs (Ry). Sometimes, the magnetic field B is given in a.u. with $B_0 = 2.3505 \times 10^9 G$.

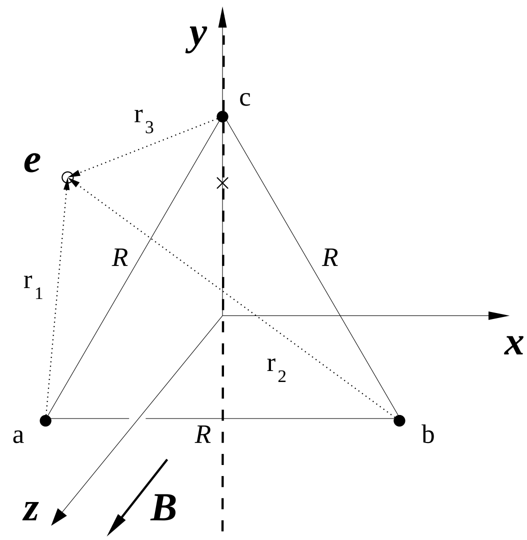

FIG. 1: Geometrical setting for the H_3^{++} ion in a magnetic field directed along the z-axis. The protons are marked by bullets and are situated in the $x-y$ plane. It is assumed that the gauge center is situated on bold-dashed line which connects the center of the triangle and the position of the proton c (see text).

II. OPTIMIZATION OF VECTOR POTENTIAL

It is well known that the vector potential for a given magnetic field, even taken in the Coulomb gauge $(\nabla \cdot \mathcal{A}) = 0$, is defined ambiguously, up to a gradient of an arbitrary function. This gives rise a feature of gauge invariance: the Hermitian Hamiltonian is gauge-independent as well as the eigenvalues and other observables. However, since we are going to use an approximate method for solving the Schroedinger equation with the Hamiltonian (1), our energies can be gauge-dependent (only the exact ones should be gauge-independent). Hence one can choose the form of the vector potential in a certain optimal way, looking for a gauge which leads to minimal energy for given class of trial functions. In particular, if the variational method is used an optimal gauge can be considered as a variational function and then is chosen by a procedure of minimization.

Let us consider a certain one-parameter family of vector potentials corresponding to a constant magnetic field B (see, for example, [4])

$$\mathcal{A} = B(-\xi(y-y_0), (1-\xi)(x-x_0), 0) \ , \tag{2}$$

where ξ, x_0, y_0 are parameters. The position of the *gauge center*, where $\mathcal{A}(x,y) = 0$, is defined by $x = x_0, y = y_0$. If the gauge center is at the origin, $x_0 = y_0 = 0$, and $\xi = 1/2$ we get the well-known and widely used gauge which is called symmetric or circular. If $\xi = 1$, it corresponds to the asymmetric or Landau gauge (see [5]). By substituting (2) into (1) we arrive at the Hamiltonian in the form

$$\begin{aligned}\mathcal{H} \ = \ & -\nabla^2 + \frac{6}{R} - \frac{2}{r_1} - \frac{2}{r_2} - \frac{2}{r_3} + 2iB[-\xi(y-y_0)\partial_x + (1-\xi)(x-x_0)\partial_y] \\ & + B^2[(1-\xi)^2(x-x_0)^2 + \xi^2(y-y_0)^2] \ , \end{aligned} \tag{3}$$

where R is the size of the triangle side.

The idea of choosing an optimal (convenient) gauge has widely been exploited in quantum field theory calculations. It has also been discussed in quantum mechanics, in particular, in connection with the present problem (see, for instance, [6] and references therein). Perhaps, the first constructive (and remarkable) attempt to apply this idea was made by Larsen [4]. In his variational study of the ground state of the H_2^+ molecular ion it was explicitly shown that gauge dependence on energy can be quite significant. Furthermore even an oversimplified optimization procedure improves the numerical results.

Our present aim is to study the ground state of (1), (3). It can be easily demonstrated that for a one-electron problem there always exists a certain gauge for which the ground state eigenfunction is a real function. Let us fix a vector potential in (1). Assume that we have solved the spectral problem exactly and have found the exact ground state eigenfunction. In general, it is a certain complex function with a non-trivial, coordinate-dependent phase. Considering their phase as gauge phase and then gauging it away, finally, it will result in a new vector potential. This vector potential has the property we want – the ground state eigenfunction of the Hamiltonian (1) is real. It is obvious that similar considerations can be performed for any excited state. In general, for a given eigenstate there exists a certain gauge in which the eigenfunction is real. These gauges can be different for different eigenstates. A similar situation takes place for any one-electron problem.

Dealing with real trial functions has an obvious advantage: the expectation value of the term $\sim \mathcal{A}$ in (1) or $\sim B$ in (3) vanishes when is taken over any real, normalizable function. Thus, without loss of generality, the term $\sim B$ in (3) can be omitted. Furthermore, it can be easily shown that, if the original problem possesses axial symmetry with axis coinciding with

the direction of the magnetic field, the real ground state eigenfunction always corresponds to the symmetric gauge.

III. CHOOSING TRIAL FUNCTIONS

The choice of trial functions contains two important ingredients: (i) a search for the gauge leading to the real ground state eigenfunction and (ii) performance of a variational calculation based on *real* trial functions. The main assumption is that a gauge corresponding to a real ground state eigenfunction is of the type (2) (or somehow is close to it)[10]. In other words, one can say that we look for a gauge of the type (2) which admits the best possible approximation of the ground state eigenfunction by real functions. Finally, in regard to our problem the following recipe of variational study is used: *First of all, we construct an* **adequate** *variational real trial function [7], which reproduces the original potential near Coulomb singularities and at large distances, where ξ, x_0, y_0 would appear as parameters. Then we perform a minimization of the energy functional by treating the trial function's free parameters and ξ, x_0, y_0 on the same footing.* In particular, such an approach enables us to find eventually the *optimal* form of the Hamiltonian as a function of ξ, x_0, y_0. It is evident that for small interproton distances R the electron prefers to be near the center of the triangle (coherent interaction with all three protons), hence x_0, y_0 should correspond to the center of the triangle. In the opposite limit of large R the electron is situated near one of the protons (a situation of incoherence - the electron selects and then interacts essentially with one proton), therefore x_0, y_0 should correspond to the position of a proton. We make a natural assumption that the gauge center is situated on a line connecting the center of the triangle and one of the protons, hence

$$x_0 = 0 \ , \ y_0 = \frac{R}{\sqrt{3}} d \ ,$$

(see Fig.1). Thus, the position of the gauge center is measured by the parameter d – the relative distance between the center of triangle and the gauge center. If the gauge center coincides with the center of the triangle, then $d = 0$. On the other hand, if the gauge center coincides with the position of proton, $d = 1$.

The above recipe was successfully applied in a study of the H_2^+-ion in a magnetic field [8] and led to prediction of the existence of the exotic ion H_3^{++} at $B \gtrsim 10^{10}\,G$ in a linear

configuration [2, 3].

One of the simplest trial functions satisfying the above-mentioned criterion is

$$\Psi_1 = e^{-\alpha_1(r_1+r_2+r_3)-B[\beta_{1x}(1-\xi)(x-x_0)^2+\beta_{1y}\xi(y-y_0)^2]}\ , \tag{4}$$

(cf. [8]), where $\alpha_1, \beta_{1x,1y}, \xi, x_0, y_0$ are variational parameters. The requirement of normalizability of (4) implies that $\alpha_1, \beta_{1x,1y}$ are non-negative numbers and $\xi \in [0,1]$. Actually, this is a Heitler-London type function multiplied by the lowest (shifted) Landau orbital associated with the gauge (2). It is natural to assume that the function (4) describes the domain of coherence - small interproton distances and probably distances near the equilibrium. Another trial function

$$\Psi_2 = \left(e^{-\alpha_2 r_1} + e^{-\alpha_2 r_2} + e^{-\alpha_2 r_3}\right) e^{-B[\beta_{2x}(1-\xi)(x-x_0)^2+\beta_{2y}\xi(y-y_0)^2]}\ , \tag{5}$$

(cf. [8]), is of the Hund-Mulliken type multiplied by the lowest (shifted) Landau orbital. Here $\alpha_2, \beta_{2x,2y},\ \xi, x_0, y_0$ are variational parameters. Presumably this function dominates for sufficiently large interproton distances R giving an essential contribution there. Hence, it models an interaction of a hydrogen atom and protons (charged centers) and can also describe a possible decay mode into them, $H_3^{++} \to H + p + p$. In a similar way one can construct a trial function which would model the interaction $H_2^+ + p$,

$$\Psi_3 = \left(e^{-\alpha_3(r_1+r_2)} + e^{-\alpha_3(r_1+r_3)} + e^{-\alpha_3(r_2+r_3)}\right) e^{-B[\beta_{3x}(1-\xi)(x-x_0)^2+\beta_{3y}\xi(y-y_0)^2]}\ . \tag{6}$$

One can say that this is a mixed Hund-Mulliken and Heitler-London type trial function multiplied by the lowest (shifted) Landau orbital. Here $\alpha_3, \beta_{3x,3y},\ \xi, x_0, y_0$ are variational parameters. It is clear that this function gives a subdominant contribution at large R and a certain, sizable contribution to a domain of intermediate distances.

There are two natural ways - linear and non-linear - to incorporate the behavior of the system both near equilibrium and at large distances in a single trial function. A general non-linear interpolation involving the above trial functions is of the form

$$\begin{aligned}\Psi_{4-1} \ = \ & \Big(e^{-\alpha_4 r_1-\alpha_5 r_2-\alpha_6 r_3} + e^{-\alpha_4 r_1-\alpha_5 r_3-\alpha_6 r_2} + e^{-\alpha_4 r_2-\alpha_5 r_1-\alpha_6 r_3} + e^{-\alpha_4 r_2-\alpha_5 r_3-\alpha_6 r_1} + \\ & e^{-\alpha_4 r_3-\alpha_5 r_1-\alpha_6 r_2} + e^{-\alpha_4 r_3-\alpha_5 r_2-\alpha_6 r_1}\Big) e^{-B[\beta_{4x}(1-\xi)(x-x_0)^2+\beta_{4y}\xi(y-y_0)^2]}\end{aligned} \tag{7}$$

(cf. [8]), where $\alpha_{4,5,6}, \beta_{4x,4y}, \xi, x_0, y_0$ are variational parameters. In fact, this is a Guillemin-Zener type function multiplied by the lowest (shifted) Landau orbital. If $\alpha_4 = \alpha_5 = \alpha_6$, the function (7) reproduces (4). While if $\alpha_5 = \alpha_6 = 0$, it reproduces (5). If $\alpha_4 = \alpha_5$ and $\alpha_6 = 0$, it reproduces (6). The linear superposition of (4), (5), (6) leads to

$$\Psi_{4-2} = A_1\Psi_1 + A_2\Psi_2 + A_3\Psi_3 \ , \tag{8}$$

where one of the parameters $A_{1,2,3}$ is kept fixed, being related to the normalization factor. The final form of the trial function is a linear superposition of functions (7) and (8)

$$\Psi_{trial} = A_1\Psi_1 + A_2\Psi_2 + A_3\Psi_3 + A_{4-1}\Psi_{4-1} \ , \tag{9}$$

where three out of four parameters A's are defined variationally. For a given magnetic field the total number of variational parameters in (9) is 20, when ξ and d are included. Calculations were performed using the minimization package MINUIT of CERN-LIB. Numerical integrations were carried out with relative accuracy $\sim 10^{-7}$ by use of the adaptive NAG-LIB (D01FCF) routine. All calculations were performed on a PC Pentium-II $450MHz$.

IV. RESULTS

Our variational study shows that in the range of magnetic fields $10^8 < B < 10^{11}\,G$ the system ($pppe$), with the protons forming an equilateral triangle perpendicular to the magnetic line, has a well-pronounced minimum in the total energy (see Table 1 and Fig. 2-5). With a magnetic field increase the total energy gets larger and the size of triangle shrinks but the height of the barrier increases (for example, it grows from ~ 0.028 Ry at 10^9 G to ~ 0.037 Ry at 10^{10} G). It was checked that the equilibrium configuration remains stable under small deviations of the proton positions but is unstable globally, decaying to $H + p + p$ and $H_2^+ + p$. This implies the existence of the molecular ion H_3^{++} in a triangular configuration for the range of magnetic fields $10^8 < B < 10^{11}\,G$.

Our calculations show that the equilibrium position always corresponds to the situation when the gauge center coincides with the center of the triangle, $d = 0$. Therefore, the optimal vector potential appears in the symmetric gauge, $\xi = 0.5$ (see Table 1 and discussion above). In Figures 2 and 5 two typical situations of absence of a bound state are presented. At $B = 10^8$ G a certain irregularity appears on the potential curve but neither $d = 1$ and

B (G)		H_3^{++}(triangle)	H_3^{++}(linear)	H-atom	H_2^+ (parallel)
	E_T (Ry)	-0.524934	—	-0.920821	-1.150697
10^9	R (a.u.)	3.161			1.9235
	ξ	0.50005			
	d	0.0			
	E_T (Ry)	2.724209	1.846367	1.640404	1.090440
10^{10}	R (a.u.)	1.4012	2.0529		1.2463
	ξ	0.50102			
	d	0.00041			
	E_T (Ry)	19.331448	16.661543	16.749684	15.522816
$5\ 10^{10}$	R (a.u.)	0.7766	1.0473		0.7468
	ξ	0.50205			
	d	0.0011			

TABLE I: Total energy, equilibrium distances and characteristics of the vector potential (2). Comparison with H_3^{++} in a linear configuration aligned along the magnetic line [3, 8], hydrogen atom [9] as well as the H_2^+-ion aligned along the magnetic line [3, 8] is given.

$d = 0$, nor d_{min} curves develop a minimum. A similar situation holds for smaller magnetic fields $B < 10^8$. At $B = 10^{11}$ G the situation is more complicated. If the gauge center is kept fixed and coincides with the center of the triangle, the potential curve displays a very explicit minimum, which disappear after varying the gauge center position (!). Something analogous to what is displayed in Fig. 5 appears for larger magnetic fields, $B > 10^{11}$ G. This artifact of the gauge center fixing at $d = 0$ had led to an erroneous statement in [1] about the existence of H_3^{++} in a triangular configuration at $B \geq 10^{11}$ G.

Fig. 3 displays the plots of different potential curves corresponding to the gauge center fixed at the position of one proton, at the center of the triangle and also varying the gauge center at $B = 10^9$ G. A curve describing the total energy demonstrates a clear, sufficiently deep minimum. As was expected small distances correspond to a gauge center coinciding with the center of the triangle, while large distances are described by a gauge center situated

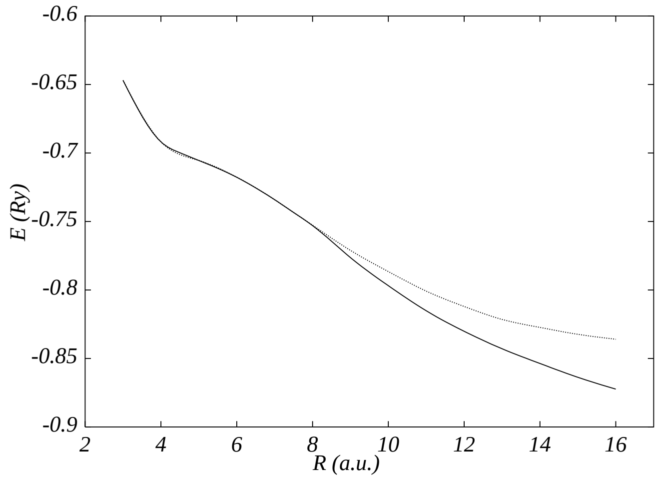

FIG. 2: Total energy of ($pppe$) at 10^8G as function of the size of the triangle (solid curve). The dotted line is a result of minimization if $d = 0$ (the gauge center coincides with the center of the triangle).

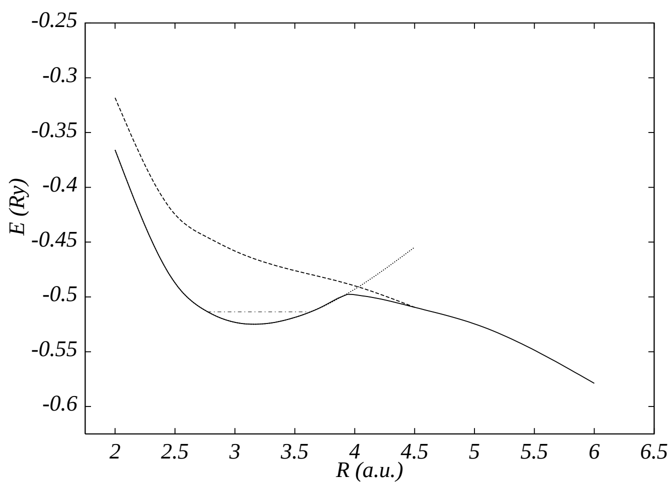

FIG. 3: Total energy of ($pppe$) at 10^9G as function of the size of the triangle (solid line). The dotted line is the result of minimization if $d = 0$ is kept fixed. The dashed line describes a result of minimization if $d = 1$ (the gauge center and position of a proton coincide, see text). The dot-dashed line displays the position of the first vibrational state.

on a proton. It is important to emphasize that the domain of near-equilibrium distances (and approximately up to the position of the maximum) is described by the gauge-center-on-center-of-triangle curve. The well keeps a vibrational state with energy $E_{vib} = 0.0112654$ Ry. In Fig.4 there are plots of different potential curves corresponding to the gauge center

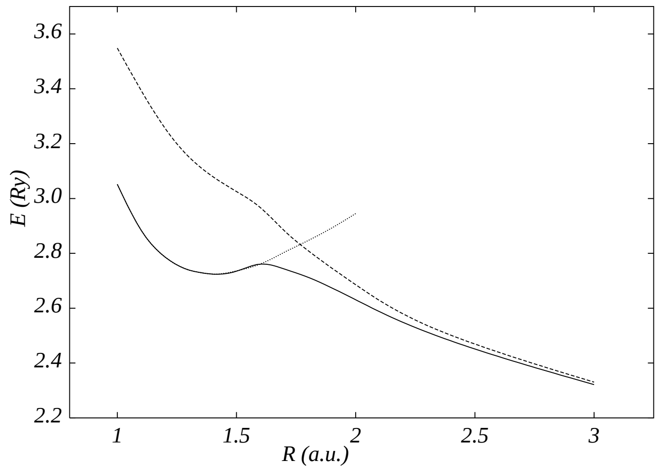

FIG. 4: Total energy of the system ($pppe$) at 10^{10}G as function of the size of the triangle (solid line). The dotted line is the result of minimization if $d = 0$ are kept fixed. The dashed line describes a result of minimization if $d = 1$ (the gauge center and position of proton coincide, see text).

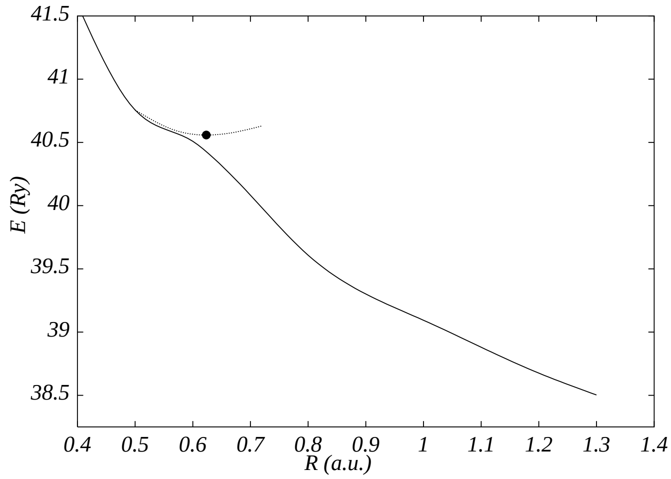

FIG. 5: Total energy of the system ($pppe$) at 10^{11}G as function of the size of the triangle (solid line). The bullet denotes the position of a spurious minimum which appear if gauge center is kept fixed at $x_0 = y_0 = 0$ ($d = 0$, dotted line) (the gauge center and the center of the triangle coincide, see [1]).

fixed at the position of one proton, at the center of the triangle and also varying the gauge center at $B = 10^{10}$ G. A curve describing the total energy demonstrates a clear, sufficiently deep minimum. Unlike the situation for $B = 10^9$ G, this well is unable to keep a vibrational state. Similar to what happens for $B = 10^9$ G, small distances correspond to a gauge center

coinciding with the center of the triangle, large distances are described by a gauge center situated on a proton, the domain of near-equilibrium distances and up to the position of the maximum is described by the gauge-center-on-center-of-triangle curve. It is quite interesting to investigate the behaviour of the gauge center position d as well as a gauge "asymmetry", ξ versus R. Both plots are of a phase transition-type, with change of behavior near the maximum of the barrier (see Figs. 6-7). The width of the transition domain is ~ 0.02 $a.u.$ (and ~ 0.1 $a.u.$ for $B = 10^{10}$ G). The evolution of the electronic distributions with respect to the size of the triangle is shown on Figs.8-9 for 10^9 G and 10^{10} G, respectively. For small and intermediate R at $B = 10^9$ G the distribution is characterized by three more or less equal peaks corresponding to the proton positions. However, it changes drastically after crossing the point of phase transition at $R \sim 3.93$ a.u. One peak disappears almost completely, while another one reduces its height. At large distances two peaks disappear completely, the distribution is characterized by one single peak, centered approximately at the position of one of the protons. For the case of $B = 10^{10}$ G the electronic distribution is always characterized by a single peak, which is situated at the center of the triangle at small and intermediate distances. Then at $R > 1.7$ a.u. the position of the peak shifts to a position of the proton. For both values of the magnetic field at asymptotically large distances the center of the peak coincides exactly with the position of the proton.

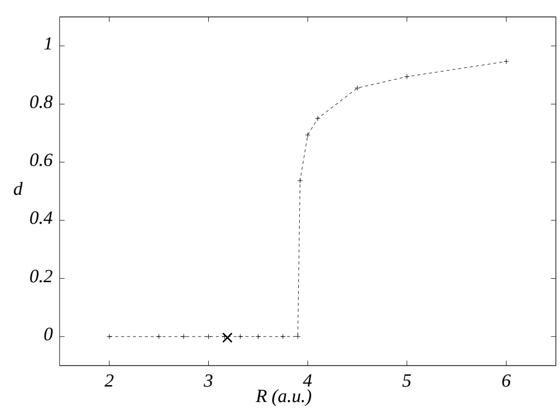

FIG. 6: Dependence of the position of the gauge center d on the size of the triangle for 10^9 G.

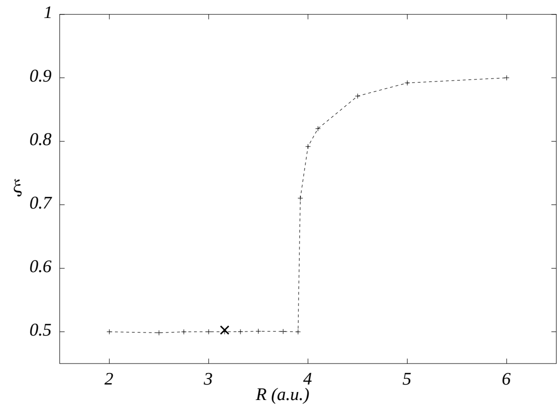

FIG. 7: Dependence of the parameter ξ on the size of the triangle for 10^9 G.

Acknowledgments

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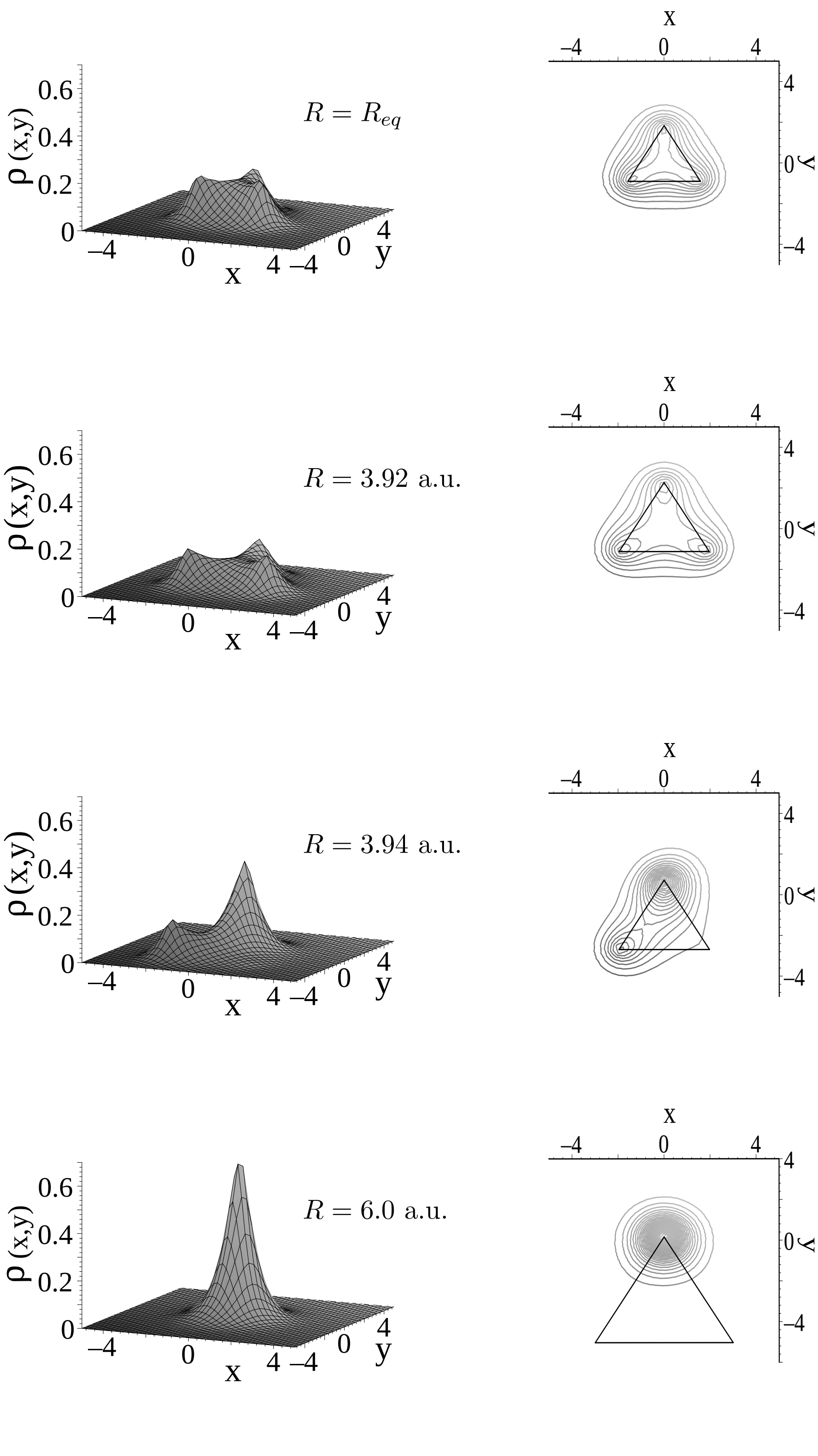

FIG. 8: Evolution with R of the integrated, normalized (to unity), electronic distributions $\rho(x,y) = \int |\Psi|^2(x,y,z)dz$ for H_3^{++} in an equilateral triangular configuration at $B = 10^9$G. The coordinates x, y are given in a.u.

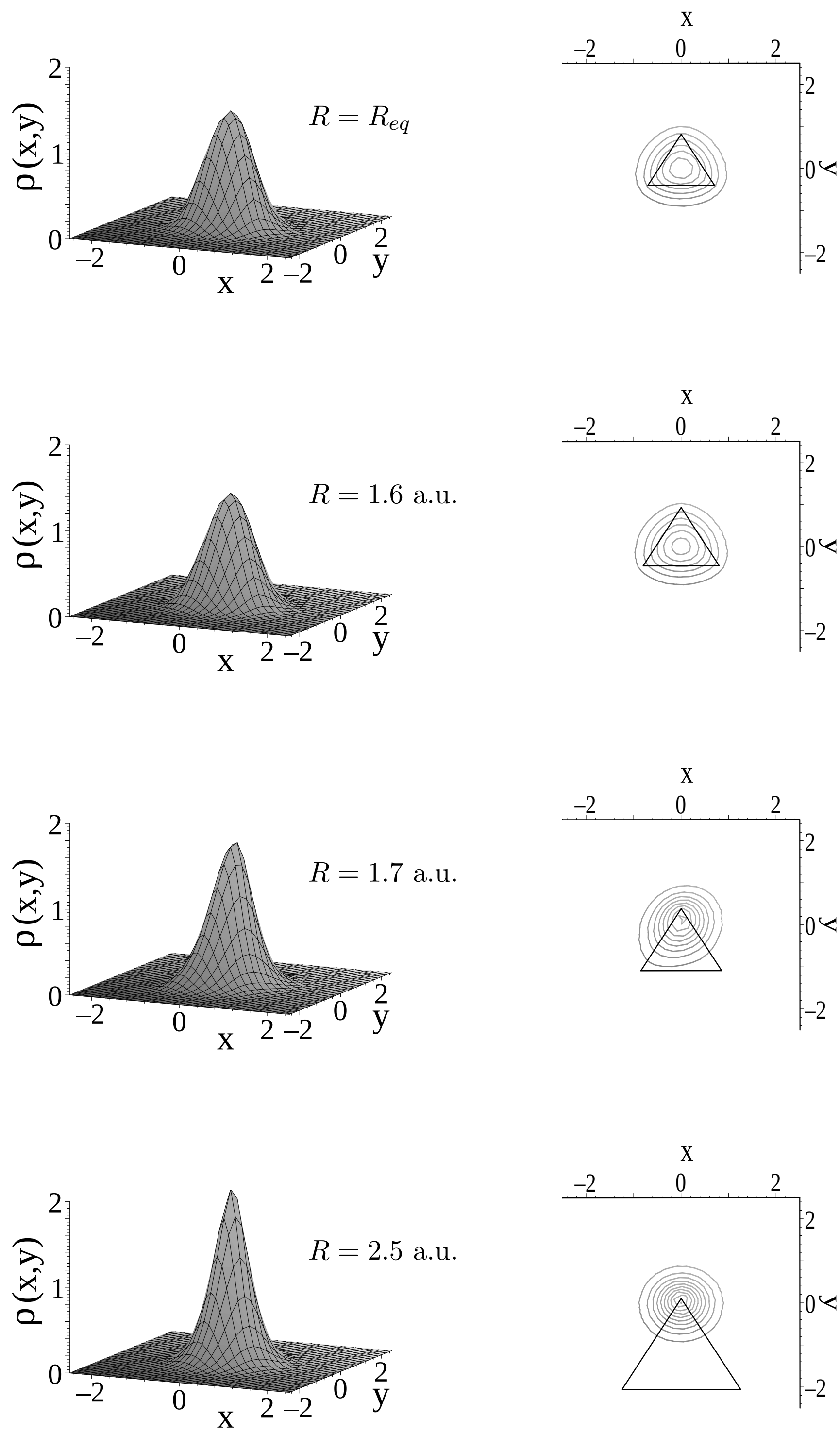

FIG. 9: Evolution with R of the integrated, normalized (to unity), electronic distributions $\rho(x,y) = \int |\Psi|^2(x,y,z)dz$ for H_3^{++} in an equilateral triangular configuration at $B = 10^{10}$G. The coordinates x, y are given in a.u.

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